

Investigation of the durability of Pt/C–RuO₂·xH₂O catalyst in PEMFC

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Abstract Pt/C–RuO₂·xH₂O catalyst was successfully prepared through the deposition of hydrated RuO₂·xH₂O on Pt/C catalyst for a proton exchange membrane fuel cell (PEMFC). The Pt/C and Pt/C–RuO₂·xH₂O catalysts were compared using physical and electrochemical techniques. The ON–OFF cycling test results showed sudden cell failures after 1,850 and 1,160 cycles for Pt/C–RuO₂·xH₂O and Pt/C, respectively. Nearly 11.2% of the cell voltage of Pt/C–RuO₂·xH₂O was lost after 1,160 cycles, compared with 26.3% for Pt/C. The charge transfer resistances of Pt/C–RuO₂·xH₂O and Pt/C increased from 0.5217 and 0.5366 Ω to 0.5732 and 0.7261 Ω , respectively. The remaining electrochemical active surface area of Pt was about 30.6% in Pt/C and about 68.9% in Pt/C–RuO₂·xH₂O after the ON–OFF test. The mean particle size of Pt/C significantly increased from 4.6 to 8.9 nm, whereas that of Pt/C–RuO₂·xH₂O increased from 4.3 to 6.3 nm. Therefore, the long-term durability of Pt/C–RuO₂·xH₂O in a PEMFC was much better than that of Pt/C.

Keywords PEMFC · Pt/C–RuO₂·xH₂O · Durability

1 Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are considered high-potential candidates for transport applications because of their high power density, low operating temperature (for fast start-up), high power-to-weight ratio, and non-requirement of corrosive fluids [1]. The 2010/2015

US Department of Energy lifetime target for automotive applications is 5,000 h, which is equivalent to 150,000 driven miles. However, the lifetime of fuel cell vehicles was approximately 1,000 h in 2008, which needs to be improved if they are to be commercialized in the near future. The durability of PEMFCs is a major barrier for the commercialization of these systems for stationary and transportation power applications [2–4].

The failure mechanisms include the ripening and compositional changes in catalysts due to corrosion, catalyst poisoning by adsorbed impurities, aging of proton exchange electrolyte membrane, changes in the hydrophobic/hydrophilic properties of catalysts, and diffusion layers. One of the most important causes of membrane electrode assembly (MEA) deterioration is the degradation of catalyst in high voltage, low pH, and oxidative environments [5, 6]. An additional embodiment to a PEMFC is the method described above, wherein, the reducing agent supplied to the cathode comprises a solid that has a standard oxidation potential less than Pt and greater than hydrogen [7]. The solid in this embodiment may be selected from a group consisting of noble metals or a group consisting of Cu, Ag, Pd, Os, Ru, and Ir. The average open-circuit voltage (OCV) of a PEMFC is almost 0.98 V [8]. RuO₂ is a highly stable transition metal oxide in an acidic environment, and its OCV is about 0.65 V [9]. Thus, the OCV of a PEMFC decreases with the Pt/C modified by RuO₂·xH₂O due to the synergistic effects of the interface between Pt and RuO₂ and the spillover of hydrogen. Therefore, decreasing the OCV improves the long-term durability of a PEMFC.

Each of the components of a PEMFC system needs to have a requisite durability to achieve durability goals. However, durability is difficult to quantify and improve primarily because of the quantity and duration (i.e., up to

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several 1000 h or more) of the necessary testing procedure [10]. To improve the durability, the degradation process of each component needs to be understood to determine possible measures for mitigating degradation and improving durability. Therefore, proper test protocols, as well as, efficient and practical tools for analyses have to be adopted. The ON–OFF cycle, which determines the lifetime of a MEA, is one of the critical parameters for evaluating possible automotive application [11]. In the current study, ON–OFF cycling tests were implemented with a single-cell configuration of 5 cm² active area until sudden cell failures. Both single electrodes and MEAs were characterized by electrochemical analysis and physical methods. *I*–*V* curves were used to examine the performance of a PEMFC. The electrodes were electrochemically measured by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Transmission electron microscopy (TEM) was used to study the particle sizes of Pt/C–RuO₂·*x*H₂O and Pt/C catalysts. These characterization methods helped to elucidate the causes of cell performance loss.

2 Experiment

2.1 Catalyst preparation

Approximately 10 mL water solution containing 5.4 mg of RuCl₃·*x*H₂O was well stirred at room temperature for 10 min. Methanol of the same volume was then added to the solution. The mixed solution was stirred for another 10 min to form the organometallic species. Approximately 20.0 mg of Pt/C catalyst (50 wt% Pt) was mixed with the prepared RuCl₃·*x*H₂O solution, and the mixture was ultrasonicated to ensure uniformity. After which, 0.1 M NaOH solution was slowly dropped into this precursor solution until a pH 7.0 was achieved. The solution was then stirred at room temperature for 30 min. The prepared precursor of the composite material was centrifugally separated and repeatedly washed with deionized water as well as ethanol until the Cl[−] content was less than 10^{−5} mol/L. The precursor was further air dried at room temperature and oven dried for 1 h at 150 °C for dehydration. After grinding in an agate mortar for 30 min, the composite material Pt/C–RuO₂·*x*H₂O catalyst (8 wt% RuO₂·*x*H₂O) was obtained. For comparison, Pt/C catalyst (50 wt% Pt) was prepared by the same procedure.

2.2 Preparation of MEA and single PEMFC

The MEA, which was composed of a Nafion-112 membrane (Dupont) and a Pt/C–RuO₂·*x*H₂O electrode for the anode and cathode, was fabricated by warming up for 60 s

and then hot pressing at 140 °C and 10 MPa for 60 s. Both cathode and anode had a Pt loading of 0.5 mg cm^{−2}. All experiments were performed using single cells with an active area of 5 cm². The MEA was mounted on a single cell with stainless steel end plates and stainless steel mesh flow fields as the current collectors.

2.3 Single cell test and ON–OFF cycling test

The performance of single cells was tested using the fuel cell test system SUN-FTP500B, which was designed and constructed by Sunrise Power Co., Ltd. The cell temperature was 60 °C. Hydrogen and air, which were employed as the fuel and oxidant, respectively, were humidified at 55 °C before being fed into the cell. The cell was maintained at a constant current density of 500 mA cm^{−2} for about 6 h until the output voltage of the cell was stable before the steady-state polarization curves were recorded.

The ON–OFF cycling test was operated by opening and closing the flow valves for the upstream and downstream of the cell until a stable cell voltage was observed. The flow rates of air and hydrogen were controlled at 2.0 and 4.0 times the stoichiometry value. Hydrogen and air were passed through humidifiers prior to being fed into the fuel cell. Fig. 1 shows the current sweep profiles applied to a single cell during the ON–OFF cycles. In the open mode (ON), hydrogen and air were supplied to the anode and cathode for 10 s, and the cell was operated at a fixed current of 4 A. In the close mode (OFF), all inlet and outlet valves were closed for 15 s. The cycling was performed until the sudden voltage drops to the initial value.

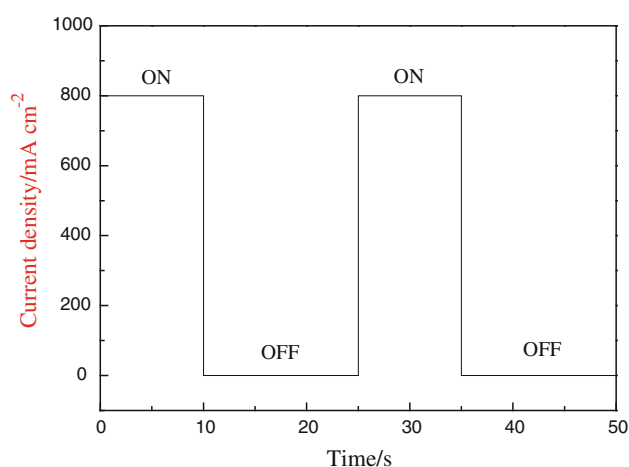


Fig. 1 Current profiles of a single cell operating under ON–OFF cycles

2.4 Electrochemical analyses

Electrochemical analyses were carried out in situ to diagnose MEA degradation before and after the ON–OFF cycles using an electrochemical analyzer system, CHI660C (CH Instruments, Shanghai, China). EIS was used to measure the ohmic resistance (R_{hr}) and charge transfer resistance (R_{ct}) of the MEAs within the frequency range of 10 kHz to 100 mHz. EIS was carried out with an applied voltage of 0.8 V, which is a potentiostatic technique. CV was used to determine the electrochemical active surface area (EAS) and hydrogen crossover current. The scanning range was limited from 0 to 1.6 V (vs. normal hydrogen electrode), and the scanning rate was 50 mV s^{-1} . The CV curves were recorded to calculate the EAS of Pt in the catalysts using the following equation [12]:

$$\text{EAS} = \frac{Q_H}{Q_{\text{ref}} L_{\text{Pt}}},$$

where Q_H is the charge of hydrogen adsorption, Q_{ref} is the charge of the monolayer adsorption of hydrogen on polycrystalline Pt [equal to $210 \text{ C (cm}^2 \text{ Pt)}^{-1}$], and L_{Pt} is the loading of Pt in the cathode. In these methods, hydrogen and nitrogen, both having a flow rate of 200 sccm were passed over the anode and cathode. The anode served as the reference and counter electrodes, and the cathode served as the working electrode.

2.5 Characterization of the MEAs by TEM

Small pieces were removed from the MEAs before and after the ON–OFF cycling tests to perform ex situ analyses including TEM. TEM measurements were carried out using a JEOL TEM 2000EX microscope operated at 120 kV and 200,000 magnification to confirm the migration of Pt particles. Samples for TEM measurements were prepared by ultrasonically suspending catalyst powder in ethanol and placing a drop of the suspension to a holey amorphous carbon film on a Cu grid.

3 Results and discussion

3.1 ON–OFF cycling test and performance of single fuel cells

Figure 2 shows the cell voltages of the different catalysts at a constant current density of 800 mA cm^{-2} during the ON–OFF cycles. The cell voltages using Pt/C– $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ and Pt/C at the beginning of the cycles are 0.37 and 0.32 V. The ON–OFF cycle tests of Pt/C– $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ and Pt/C show sudden cell failures after 1,850 and 1,160 cycles. The voltage losses of the single cells caused by the ON–OFF

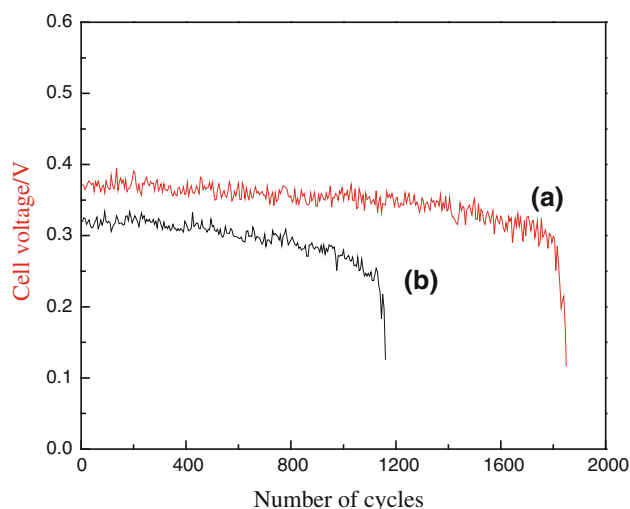


Fig. 2 Cell voltage as a function of the number of cycles measured at 800 mA cm^{-2} : (a) Pt/C– $\text{RuO}_2 \cdot x\text{H}_2\text{O}$, and (b) Pt/C

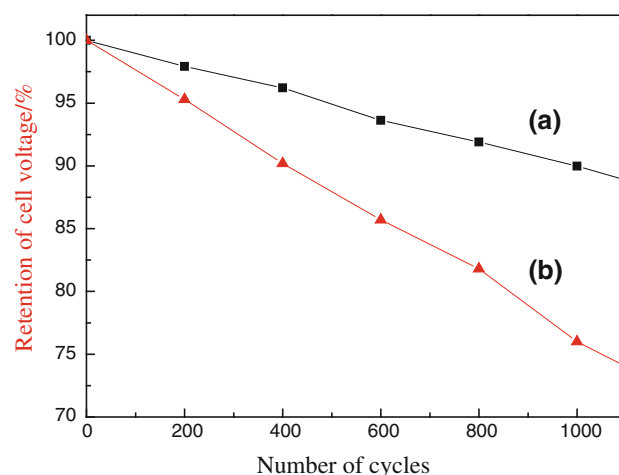


Fig. 3 Comparison of retention of cell voltage of Pt/C– $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ (a) and Pt/C (b) electrodes under different numbers of ON–OFF cycles

cycles are recorded with respect to the number of ON–OFF cycles (Fig. 3). The voltage loss of the cell using Pt/C is much larger than that using Pt/C– $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ at the same number of ON–OFF cycles. The different decay rates obtained from the ON–OFF cycle tests are considered to be the different degradation mechanisms of the MEA.

The I – V curve of the single cell was first measured before the ON–OFF cycles. The degradation rate of the single cell can be calculated using the following equation:

$$\text{Degradation rate (mV cycle}^{-1}\text{)} = \frac{\text{original performance (mV)} - \text{final performance (mV)}}{\text{cycle number}}.$$

The I – V curves of the single cells employing the Pt/C and Pt/C– $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ catalysts are shown in Fig. 4. The initial

cell performance using Pt/C–RuO₂·xH₂O is slightly better than that using Pt/C. The OCV of Pt/C and Pt/C–RuO₂·xH₂O is 0.947 and 0.887 V, respectively. However,

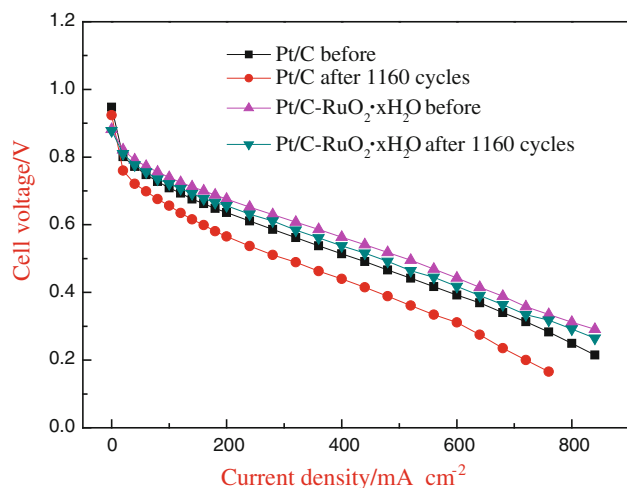


Fig. 4 Performances of PEMFC single cells

the cell performance after the ON–OFF cycles using Pt/C–RuO₂·xH₂O is much better than that using Pt/C. For example, the voltage loss of the cell using Pt/C–RuO₂·xH₂O at 600 mA cm^{−2} is 25 mV after the ON–OFF cycles (the overall decay rate is 0.0216 mV cycle^{−1}), which is much lower than that using Pt/C (105, 0.0698 mV cycle^{−1}, respectively). Both catalysts gradually decrease as the potential scan proceeds. Nearly 11.2% of the cell voltage using Pt/C–RuO₂·xH₂O is lost after 1,160 cycles, compared with 26.3% using Pt/C. Hence, Pt/C–RuO₂·xH₂O has the lower decreasing rate.

Table 1 Calculated values obtained from the equivalent circuit

	$R_{\text{hf}} (\Omega)$	$R_{\text{ct}} (\Omega)$
Pt/C (before 1,160 cycles)	0.3299	0.5366
Pt/C (after 1,160 cycles)	0.3793	0.7261
Pt/C–RuO ₂ ·xH ₂ O (before 1,160 cycles)	0.3067	0.5214
Pt/C–RuO ₂ ·xH ₂ O (after 1,160 cycles)	0.3224	0.5732

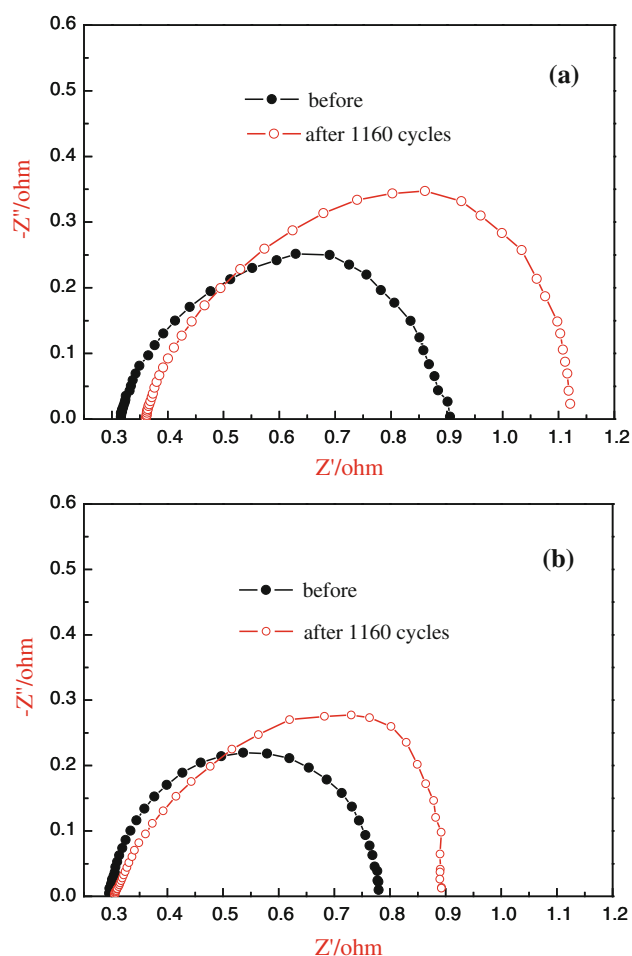


Fig. 5 Electrochemical impedance spectra of the MEA with **a** Pt/C and **b** Pt/C–RuO₂·xH₂O before and after 1,160 cycles

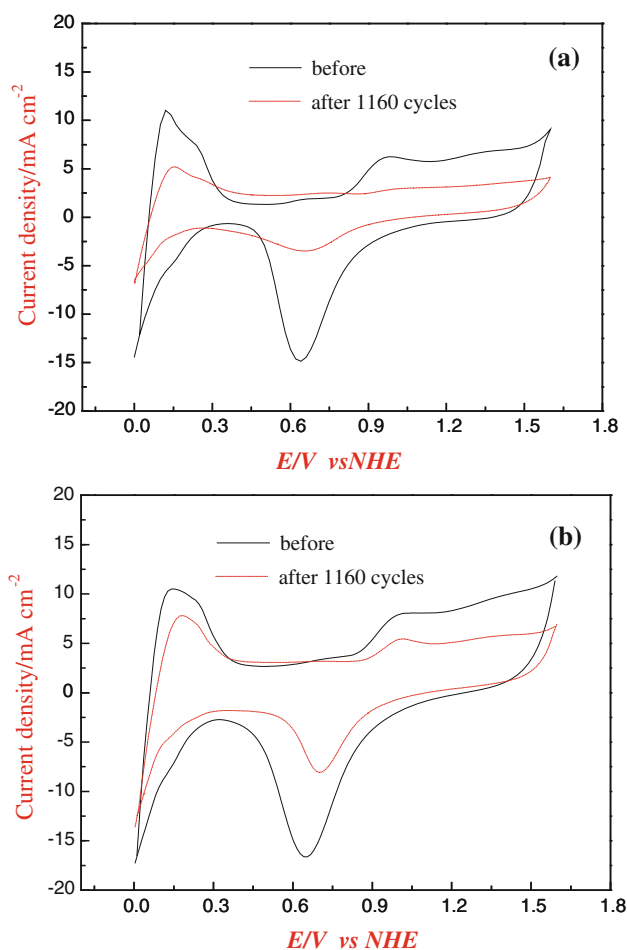


Fig. 6 Cyclic voltammograms of the MEA with **a** Pt/C and **b** Pt/C–RuO₂·xH₂O before and after 1,160 cycles

3.2 Chemical and physical analysis

EIS was performed to investigate the characteristics of the proton transfer at the polymer electrolyte membrane and the charge transfer at the catalyst/electrolyte interface that limits possible MEA degradation during operation [13]. Figure 5 shows the Nyquist plots for the single cells measured at 0.8 V. For all single cells, the Nyquist plots have semicircles with the ohmic resistance (R_{hf}) at the

Table 2 Electrochemical active surface area (EAS) of Pt/C and Pt/C–RuO₂·xH₂O catalysts

Catalyst	EAS before 1,160 cycles (m ² g ^{−1} Pt)	EAS after 1,160 cycles (m ² g ^{−1} Pt)	EAS remaining (%)
Pt/C	73.8	22.6	30.6
Pt/C–RuO ₂ ·xH ₂ O	78.1	53.8	68.9

intercept of the x -axis at high frequencies, and the charge transfer resistance (R_{ct}) is the width of the semicircle. The corresponding equivalent circuits are developed by simulating the impedance spectra using the Zsimpwin software. The calculated parameters of the equivalent circuit are listed in Table 1. At the end of 1,160 cycles, R_{hf} of Pt/C–RuO₂·xH₂O and Pt/C tremendously increased from 0.3067 and 0.3299 Ω to 0.3224 and 0.3793 Ω , respectively. These results may be due to the membrane degradation during the ON/OFF cycles. However, R_{ct} increased from 0.5217 and 0.5366 Ω to 0.5732 and 0.7261 Ω . This result implies that the addition of RuO₂·xH₂O causes R_{ct} to decline, reflecting a faster reactive velocity. Consequently, the steady-state performance increases when RuO₂·xH₂O is added to the cathode of the single cell.

The CV curves of the thin film electrodes fabricated using Pt/C and Pt/C–RuO₂·xH₂O catalysts are shown in Fig. 6. The CV curves present well-shaped current peaks corresponding to the adsorption/desorption of hydrogen on

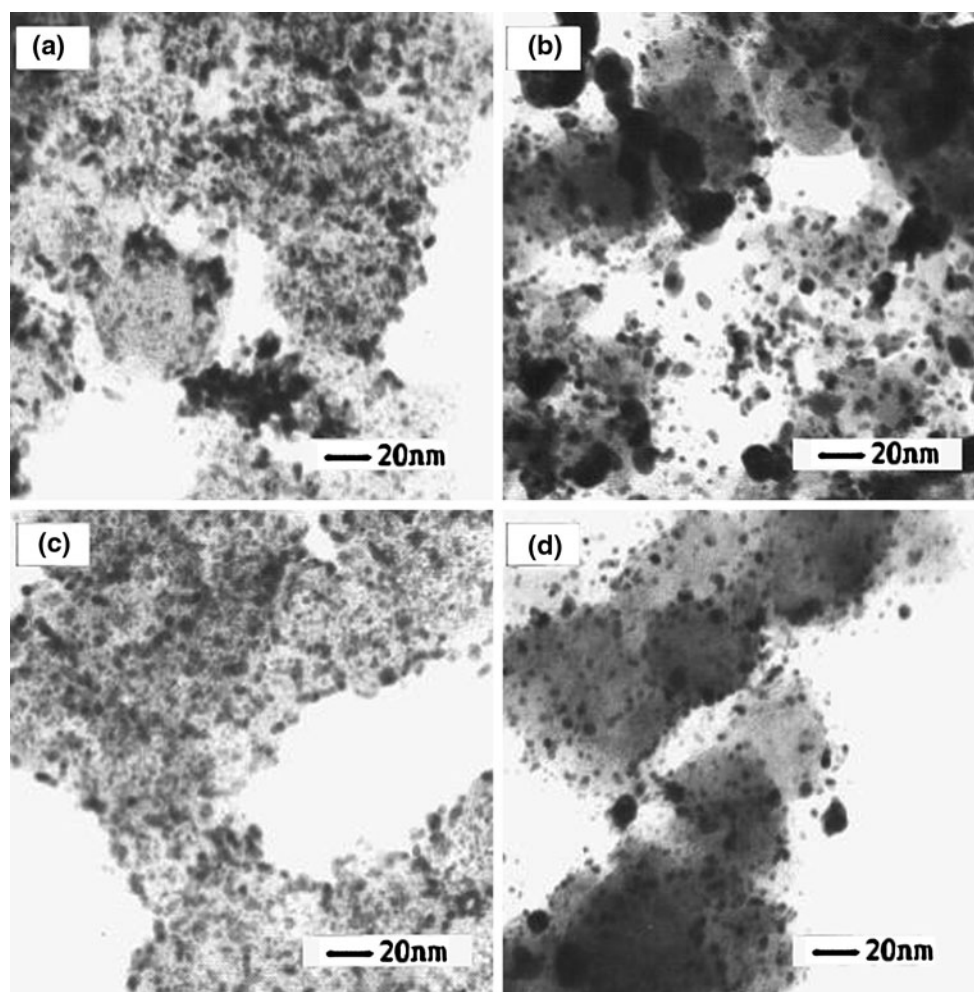


Fig. 7 TEM image of the catalysts. Pt/C catalyst **a** before ON–OFF and **b** after ON–OFF; Pt/C–RuO₂·xH₂O catalyst **c** before ON–OFF and **d** after ON–OFF

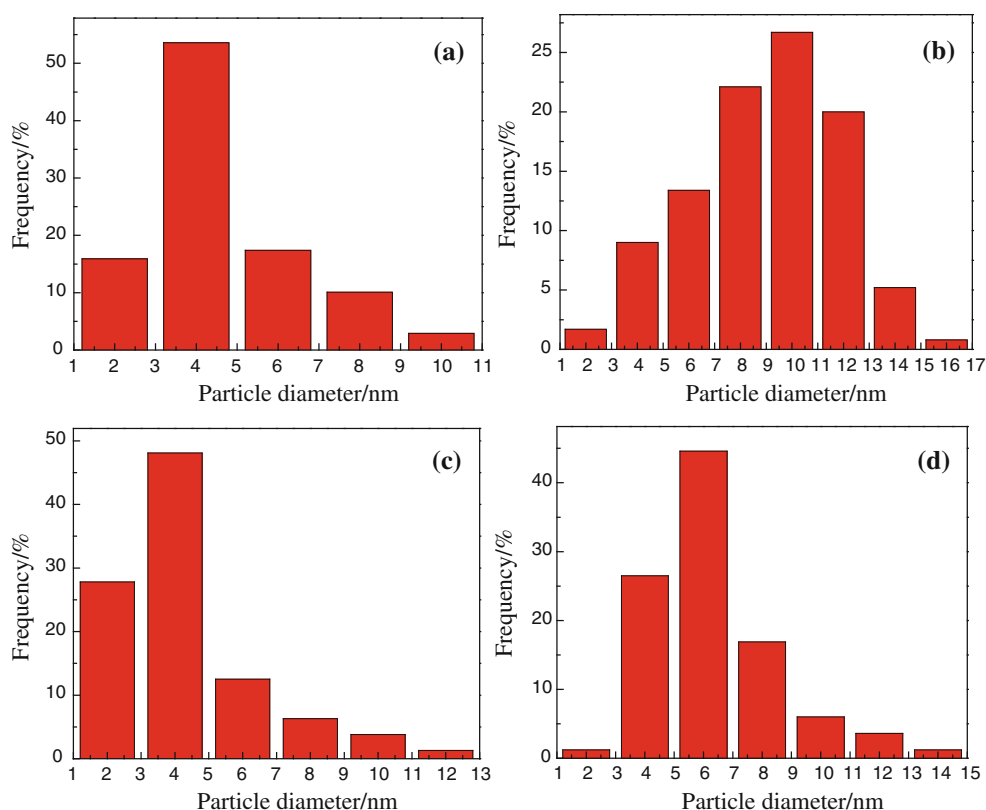


Fig. 8 Histograms of the particle size distributions of the catalysts. Pt/C catalyst **a** before ON–OFF and **b** after ON–OFF; Pt/C–RuO₂·xH₂O catalyst **c** before ON–OFF and **d** after ON–OFF

the Pt surface, and the oxidation/reduction of the oxygen-containing species on the same surface [14]. The EAS of Pt in the catalyst is calculated as described in Table 2. The initial EAS value of Pt in Pt/C–RuO₂·xH₂O before the ON–OFF cycle is 78.1 m² (g_{Pt})^{−1}, which is larger than that of Pt in Pt/C 73.8 m² (g_{Pt})^{−1}. The EAS value of Pt in Pt/C is reduced to 22.6 m² (g_{Pt})^{−1} after 1,160 ON–OFF cycles. The remaining EAS of Pt in Pt/C after the ON–OFF cycle is about 30.6%. By contrast, the EAS of Pt in Pt/C–RuO₂·xH₂O is 53.8 m² (g_{Pt})^{−1} after the ON–OFF cycle, which is obviously larger than that of Pt in Pt/C. The remaining EAS of Pt in Pt/C–RuO₂·xH₂O is about 68.9%. These results indicate that Pt/C–RuO₂·xH₂O catalyst is more durable than Pt/C catalyst.

Figures 7 and 8 show the TEM images and distributions of Pt particle size before and after the ON/OFF cycles. The results indicate that the dispersion of Pt particles in both Pt/C–RuO₂·xH₂O and Pt/C is uniform before the ON/OFF cycles. The mean particle size is around 4.6 nm for Pt/C and 4.3 nm for Pt/C–RuO₂·xH₂O. Obvious agglomeration and coalescence of Pt particles in Pt/C are observed after the ON/OFF cycles (Fig. 7b). The mean particle size of Pt increases to 8.9 nm with a broad size distribution. However, the mean particle size of Pt in Pt/C–RuO₂·xH₂O increased to 6.3 nm, which is much smaller than that in Pt/C. The size distribution

of Pt particles in Pt/C–RuO₂·xH₂O remains approximately uniform [15]. Therefore, the long-term durability of the morphology of Pt/C–RuO₂·xH₂O is much better than that of Pt/C when they are used as PEMFC catalysts.

4 Conclusions

In the current paper, Pt/C–RuO₂·xH₂O and Pt/C catalysts were evaluated and compared. A MEA durability test under the ON–OFF cycling protocol was performed. Physical and electrochemical techniques were applied to investigate the structure, performance, and durability of the catalysts. The EAS loss, particle size distribution, polarization behavior, and electrochemistry impedance spectra suggested that Pt/C–RuO₂·xH₂O showed a better durability than Pt/C.

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References

1. Wu JF, Yuan XZ, Wang HJ (2008) Int J Hydrogen Energy 33:1735

2. Wang ZB, Zou PJ, Chu YY, Shao YY, Yin GP (2009) Durability studies on performance degradation of Pt/C catalysts of proton exchange membrane fuel cell. *Int J Hydrogen Energy* 34:4387
3. Zhang SS, Yuan XZ, Wang HJ, Mérida W, Zhu H, Shen J et al (2009) A review of accelerated stress tests of MEA durability in PEM fuel cells. *Int J Hydrogen Energy* 34:388
4. Zhang SS, Yuan XZ, Hin JNC, Wang HJ, Andreas Friedrich K, Schulze M (2009) A review of platinum-based catalyst layer degradation in proton exchange membrane fuel cells. *J Power Sources* 194:588
5. Liu D, Case S (2006) Durability study of proton exchange membrane fuel cells under dynamic testing conditions with cyclic current profile. *J Power Sources* 162:521
6. Debe MK, Schmoeckel AK, Vernstrom GD, Atanasoski R (2006) *J Power Sources* 161:1004
7. Zhaoa D, Yia BL, Zhang HM, Yu HM (2010) MnO₂/SiO₂-SO₃H nanocomposite as hydrogen peroxide scavenger for durability improvement in proton exchange membranes. *J Membr Sci* 346:143
8. Janssen GJM, Sitters EF, Pfrang A (2009) Proton-exchange-membrane fuel cells durability evaluated by load-on/off cycling. *J Power Sources* 191:501
9. Wu XX, Xu HF, Lu L, Fu J, Zhao H (2010) The study on dynamic response performance of PEMFC with RuO₂·xH₂O/CNTs and Pt/C composite electrode. *Int J Hydrogen Energy* 35:2127
10. Borup RL, Davey JR, Garzon FH, Wood DL, Inbody MA (2006) PEM fuel cell electrocatalyst durability measurements. *J Power Sources* 163:76
11. Seo D, Lee J, Park S, Rhee J, Won Choi S, Shul Y-G (2011) Investigation of MEA degradation in PEM fuel cell by on/off cyclic operation under different humid conditions. *Int J Hydrogen Energy* 36:1828
12. Liu X, Chen J, Liu G, Zhang L, Zhang HM, Yi BL (2010) Enhanced long-term durability of proton exchange membrane fuel cell cathode by employing Pt/TiO₂/C catalysts. *J Power Sources* 195:4098
13. Prasanna M, Cho EA, Lim T-H, Oh I-H (2008) Effects of MEA fabrication method on durability of polymer electrolyte membrane fuel cells. *Electrochim Acta* 53:5434
14. Zhou ZM, Shao ZG, Qin XP, Chen XG, Wei ZD, Yi BL (2010) Durability study of Pt–Pd/C as PEMFC cathode catalyst. *Int J Hydrogen Energy* 35:1719
15. Xie J, Wood DL III, More KL, Atanasov P, Borup RL (2005) Microstructural changes of membrane electrode assemblies during PEFC durability testing at high humidity conditions. *J Electrochem Soc* 152(2005):A1011